

Aluminum negative electrode in lithium ion batteries

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Abstract

In search of new non-carbonaceous anode materials for lithium ion batteries, aluminum has been tested as a possible candidate. In order to examine the intrinsic properties of this metal versus a lithium electrode at 293 K, aluminum thin films have been deposited by thermal evaporation and characterized. Capacities of 1000 mAh/g have been measured in films with thickness ranging from 0.1 to 1 μ m. These capacities are probably due to the formation of amorphous Li-Al alloys as indicated by X-ray diffraction analysis and electrochemical measurements. The huge stress induced by volume changes upon cycling has been evidenced by scanning electron microscopy observations. The thinnest samples are the less damaged after the electrochemical tests. Despite a huge loss in capacity due to volume changes in the electrode upon cycling, aluminum appears as a good material as a negative electrode for lithium ion batteries.
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1. Introduction

Recently, tin has been proposed as a good candidate to replace graphite as a negative electrode for lithium ion cells [1–4]. The main advantage of tin compared to standard graphite is its high mass and volume capacities, respectively, 994 mAh/g and 7254 mAh/cm³. Not only tin is able to form alloys with lithium. Bi, Si or Al for example, can also react with lithium to form intermetallic compounds [5–7]. Aluminum and LiAl alloys have been extensively studied as a possible anode to replace lithium in lithium batteries since the early 70's [2,8]. However, the use of this metal in a lithium ion battery has been rarely envisioned [9]. An observation of the Al-Li binary diagram indicates that there are three possible alloys, AlLi, Al₂Li₃, Al₄Li₉ [10]. Therefore, the maximum theoretical lithium uptake for an aluminum electrode will be 2.25 Li for each Al atom. This value is below the 4.4 Li for each Sn atom observed in the Li₂₂Sn₅ alloy. However, due to its low atomic weight compared to tin, aluminum can present a mass capacity of 2234 mAh/g if the Al₄Li₉ alloy is reached, which is more than twice the theoretical capacity of metallic tin. Even for the LiAl alloy, the theoretical capacity is 993 mAh/g. Therefore, aluminum

based compounds seem of great interest as potential anode materials for Li-ion cells. In this study, only the metal itself has been investigated versus a lithium electrode. In order to avoid the contribution of binder or conductive additive in the electrochemical tests, we have focused our interest on aluminum thin films.

2. Experimental

Aluminum layers ranging from 0.1 to 1 μ m have been deposited by thermal evaporation of aluminum granules on copper substrates. Deposition was performed when the remaining pressure in the vacuum chamber was less than 10⁻³ Pa. The crystallinity of the samples was checked using a PW1710 Philips diffractometer. The thickness of the films were checked by using a Dektak 3st profilemeter. The weight was determined by using a Mettler Ag245 balance (0.01 mg accuracy).

For both potentiostatic and galvanostatic tests, the films have been used "as-deposited", i.e. without the use of any binder or conductive additive. All the samples have been cycled versus a metallic lithium electrode in LiPF₆ in 2:1 EC:DMC electrolyte. The voltage limits were set at 10 mV versus Li (reduction) and 1.2 V versus Li (oxidation) for the discharge and the charge, respectively. The cycling rate was

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10 mV/120 s for the cyclic voltammetry experiments and C/4 rate for the galvanostatic experiments. For the determination of the diffusion coefficient of Li in LiAl, the sweep rate has been varied according to the method described in ref. [11].

The observation of the microstructure was performed using a LEICA 440 stereoscan scanning electron microscope (SEM) coupled with a energy dispersive X-ray (EDX) analysis.

3. Results and discussion

All the samples are well crystallized according to the X-ray diffraction patterns (XRD) as shown in Fig. 1a. In all the diagrams, only the (1 1 1) reflection of aluminum is detected, thus indicating that the films have grown in a preferential orientation.

The electrochemical activity of aluminum is clearly evidenced on the cyclic voltamogram (Fig. 2) where sharp peaks are observed both during the charge and the discharge.

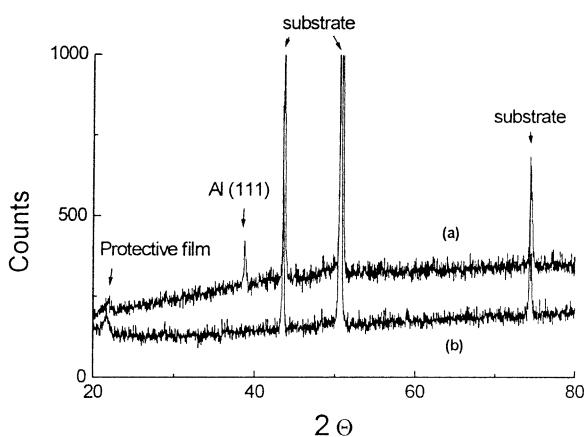


Fig. 1. X-ray diffraction pattern of an aluminum thin film (0.3 μm): (a) as-deposited; (b) at the end of the discharge (0.01 V/Li).

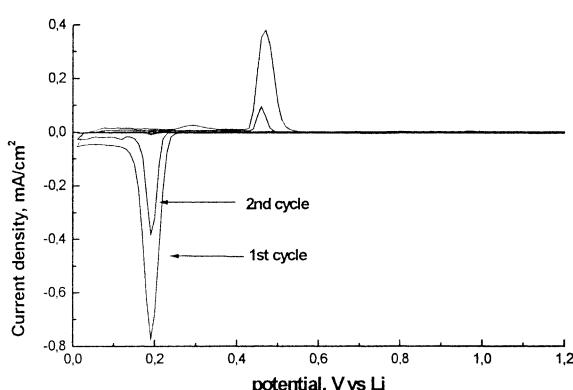


Fig. 2. Typical cyclic voltamogram of an aluminum thin film (0.3 μm , 10 mV/120 s, 1.2–0.01 V).

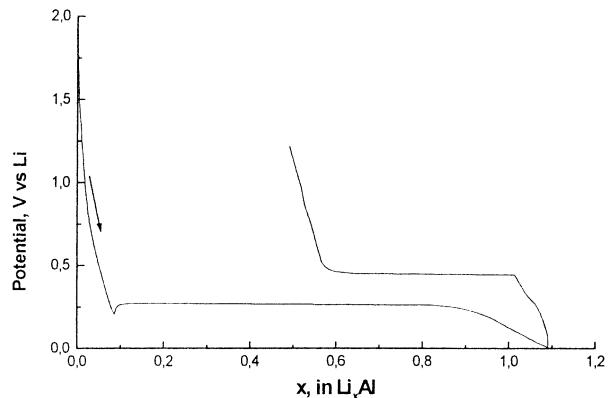


Fig. 3. Typical galvanostatic plot of an aluminum thin film (0.3 μm , C/4 rate, 1.2–0.01 V).

On the galvanostatic plot (Fig. 3), it can be seen that the charge mainly consists in three regions, the initial lithium “insertion” between 2 and 0.26 V, followed by a wide plateau at 0.26 V, and a final “insertion” occurring between 0.26 and 0.01 V. The penalty in voltage reduction (average voltage of 0.26 V versus lithium) is acceptable compared to graphite anodes.

The lithium uptake on the first voltage region (I) is related to the presence of an oxidized layer on the top of the aluminum thin films. This layer has been evidenced by X-ray photoelectron spectroscopy (XPS) and its role is currently under examination. Rough calculation of the lithium inserted between 2 and 0.26 V shows that it is directly related to the reduction of the oxidized aluminum species. Since the oxidized layer remains constant in all the films, it seems reasonable that the contribution of the first voltage region to the overall lithium uptake becomes smaller as the total thickness of the film is increased. At the end of this first lithium uptake (region I, Fig. 3), no change is observed in the XRD patterns.

Table 1 summarizes the capacities of different aluminum thin films in the 3 voltage regions described above. The expected theoretical capacities for the formation of LiAl is 993 mAh/g. The capacity values in Table 1 show that the plateau at 0.26 V versus Li (region II) can be assigned to the formation of the LiAl alloy. However, the lithium uptake in region III (between 0.26 V and 10 mV versus Li) does not lead to the formation of the lithium richest alloy Li_9Al_4 .

During the discharge and the charge of the thin film electrodes, structural and microstructural changes occur in the film. On the XRD patterns, the (1 1 1) reflection due to the crystallized aluminum layer have disappeared at the end of the discharge (Fig. 1b). There is no additional reflection indicating that crystallized Li-Al alloys have formed. At the end of the charge, where the Li-Al alloys are supposed to decompose, the recrystallization of aluminum is not observed.

The observations by scanning electron microscopy reveal microcracks in all the samples after one complete cycle. However the surface of the thinnest sample (0.1 μm) seems

Table 1

First charge and discharge capacities of aluminum thin films (region I: 2–0.26 V vs. Li; region II: plateau at 0.26 V vs. Li; region III: 0.26–0.01 V vs. Li)

Thickness (μm)	Region I (mAh/g)	Region II (mAh/g)	Region III (mAh/g)	Q_{charge} (mAh/g)	$Q_{\text{discharge}}$ (mAh/g)	$Q_{\text{discharge}}/Q_{\text{charge}}$ (%)
0.1	250	890	250	1390	800	58
0.3	80	810	200	1090	610	56
1	10	690	260	960	420	44

less damaged than the 0.3 and 1 μm layers and it is not surprising that the highest capacity is measured for the 0.1 μm sample. Furthermore, this sample presents the best charge to discharge ratio (Table 1) and subsequently the lowest capacity fade upon cycling. If the LiAl alloy is formed, the volume of the initial aluminum electrode is doubled. The mechanical stress induced by this volume change will be more easily accommodated in the thinnest films, which can explain the microstructural differences between the SEM observation of 0.1 and 1 μm thick films.

The lithium diffusion coefficient in LiAl has been estimated according to ref. [11]. In the potentiostatic mode, the sweep rate was varied from 0.02 to 0.33 mV/s. The change in the peak current dependence of the sweep rate occurs around 0.1 mV/s, which was taken as the critical sweep rate. Therefore, the calculation of the lithium diffusion coefficient gives a value of $6 \times 10^{-12} \text{ cm}^{-2}/\text{s}$ at 293 K. This value is at least two orders of magnitude lower than the chemical diffusion coefficients of some lithium alloy phases reported by R.A. Huggins in [4], especially Li–Sn alloys.

Despite the low diffusion coefficient of Li in the LiAl alloy, different aluminum thin films have exhibited capacities close to 1000 mAh/g at C/4 rate. This suggests that further investigation of aluminum based compounds must be done. Now that the electrochemical behavior of pure aluminum thin films have been determined, it should be interesting to test an aluminum powder in an adequate matrix with binders and conductive additives.

4. Conclusions

In order to test aluminum as a possible anode material for lithium ion batteries, thin films of this metal have been deposited and characterized. The discharge curves have shown that there are mainly three voltage regions corresponding to different electrochemical reactions. The first one takes place between 2.6 and 0.26 V and is assigned to the reduction of the oxidized aluminum layer on the top surface of the films. The plateau at 0.26 V versus Li can be assigned

to the formation of LiAl. However there is no structural evidence that this alloy is formed on the XRD pattern and therefore, it is supposed that it might be an amorphous compound. The last region down to 10 mV versus Li does not lead to the formation of the lithium richest aluminum alloy Li₉Al₄.

A loss in capacity is systematically observed in the films, probably due to the expansion of the electrode upon cycling. However, the aluminum thin films have shown capacities close to 1000 mAh/g. This suggests that aluminum can be a possible candidate as a negative electrode for Li ion cells if an adequate matrix is determined in order to optimize the stability upon cycling and to decrease the capacity fade.

Ongoing studies on aluminum powders will provide additional information on the possible use of aluminum as negative electrode in lithium ion cells.

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